NDE OF POLYMER COMPOSITES USING MAGNETIC RESONANCE TECHNIQUES

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Polymer based materials have become increasingly important in structural applications primarily due to their high strength to weight ratio. As the use of polymer-based composites has increased, so has the need for reliable non-destructive evaluation techniques. In this paper, a new NDE method for these materials is proposed. The technique relies on the observation of an electron paramagnetic resonance (epr) absorption at the site of damage in a polymer. Using applied magnetic field gradients the physical location of damage can be discerned and an image of the damage site can be obtained. This should allow the detection of cracks and delaminations with high resolution, good sensitivity and good contrast.

The foundations for epr spectroscopy rest on the interaction of unpaired electron spins with an applied magnetic field. In zero field the energy levels of the "free" electron are degenerate. As a field is applied the energy levels are Zeeman split with the energy difference increasing linearly with the strength of the field (see Fig. 1(a)). The substance with "free" electrons is placed in a microwave system of fixed frequency and the magnetic field is swept; as the energy difference of the electron states is increased it will at one point match the energy of the applied microwave field. At that point a resonant absorption of microwave energy will result (see Fig. 1(b)). The equation governing the absorption is $\Delta E = g\beta H_o = h\nu$ where β is the Bohr magneton, H_o is the resonant magnetic field, h is Planck's constant and ν is the microwave frequency. The resonance is characterized by the g factor which gives information as to the nature of the free radical, the linewidth ΔH_{pp} which is informative as to the dynamics of spin relaxation and the integrated intensity I which is proportional to the number of spins. In practice, the magnetic field is modulated, phase sensitive detection is used and the first derivative of absorption is displayed. The result for the simplest case is shown in Figure 2.

It has previously been shown [1,2,3] that epr signals are generated when polymeric materials are damaged. The mechanism for generating free spins is the breaking of polymer bonds. For each bond cleaved, two free radicals are formed. These species by nature are highly reactive and prone to recombination such that the intrinsic free radical has a very short lifetime. However, species that interact with the primary radicals

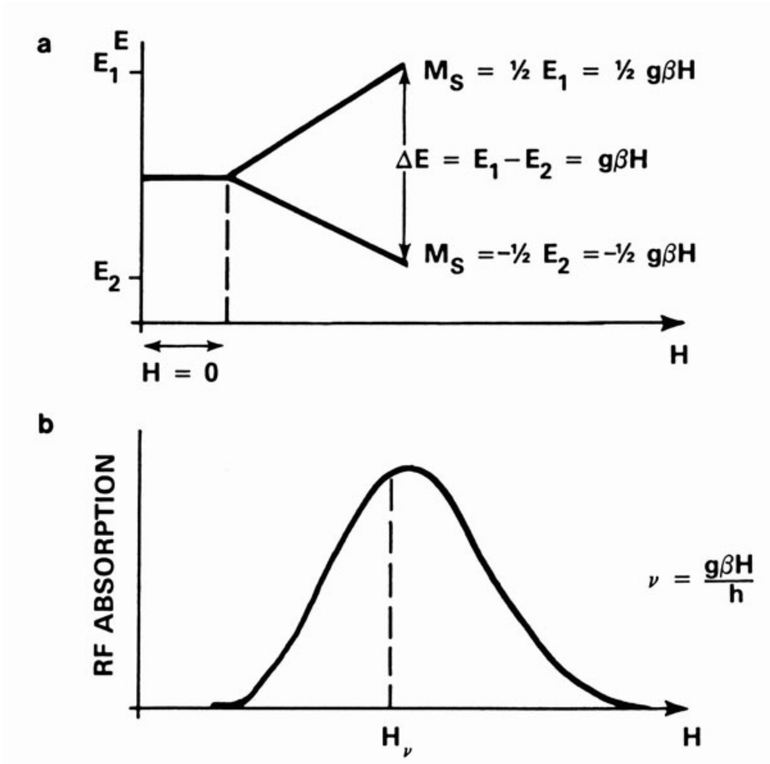


Fig. 1 a) Energy levels of a "free" electron in a magnetic field illustrating Zeeman splitting.
b) Microwave absorption for a free electron as a function of applied field.

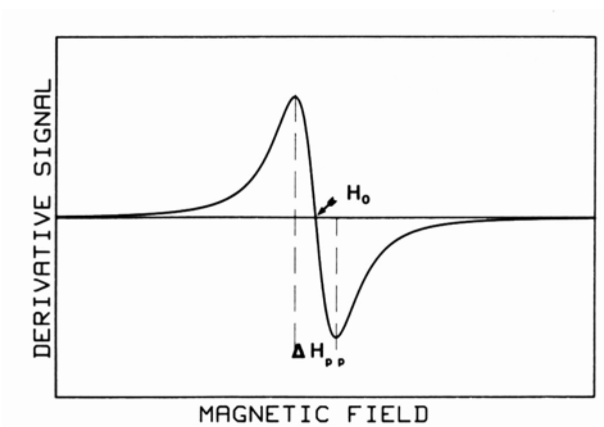


Fig. 2 EPR signal for an ideal free radical with Lorentzian lineshape.

often become paramagnetic and secondary or tertiary free radical species can be observed.

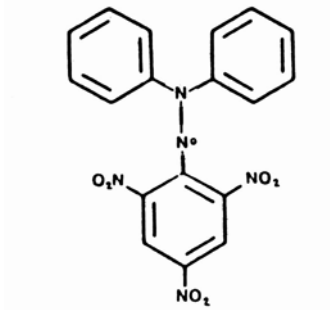
We have previously shown that stable epr signals could be generated in nylon that has been damaged by mechanical stress [2]. It was postulated that the free radicals were trapped by inorganic impurities present in the nylon, due to the high g-value and broadness of the line. This was borne out by later experiments where organic spin traps were added to the fibers. In this case all of the free radicals were preferentially trapped by the strong electron acceptor that was added. This led to a very well conditioned epr signal, with the integrated intensity tracking with the stress on the fibers [3].

These results allowed the quantification of the integrated (over time and space) amount of damage in a polymer sample. This did not give information, on a local scale, as to the topography of the damage. A single large crack would, using this technique, give the same signal as the equivalent number of small cracks. It was therefore necessary to impart spatial sensitivity to the epr signal.

This is achieved by adding magnetic field gradient coils to the instrument. The effect of these coils is to add a linear magnetic field gradient to the sample such that the applied field becomes $H = H_o + Gx$ where H_o is the applied field without the gradient, G is the gradient strength and x is a positional variable. The analogous techniques using nuclear magnetic resonance (NMR) have become widely used in the biomedical community since the first report of NMR imaging by Lauterbur [4]. We feel that epr techniques have significant advantages over NMR techniques in solid samples.

To illustrate the technique, samples were made with various spin phantoms. Small (~ 100 micron) spots of the stable organic free radical DPPH (Fig. 3) were placed on a quartz holder in the epr cavity. The quartz holder was attached to a goniometer to allow accurate values of rotation angle. The dashed line of Figure 4 shows a spectrum taken of a simple two spot phantom without an applied gradient. The separation between the two spots is ~ 3 mm and one spot is about twice as large as the other. This spectrum is similar to Fig. 2 and is what is typically observed for solid state free radicals. The solid line of Figure 4 shows the effect of an applied field gradient of 9.5 G/cm on the sample. The single peak has split into two peaks due to the two sites of spin density. The spectrum shows two clearly resolved lines with intensity ratios of approximately 2:1. The separation in magnetic field between the two peaks can be related back to the spatial separation by using the known field gradient. The separation between the peaks in a sample is dependent on the angle (θ) that the sample plane makes with the field gradient direction. In Fig. 5 the peak separation is plotted as a function of cos θ. The straight line obtained indicates that the projection of spin density on the gradient axis is indeed generated by sample rotation. If a series of rotations is carried out, an image of the spin density in an object can be generated.

The generation of the spin density profiles in a real object can become somewhat complicated by the non-ideal lineshape exhibited by some samples. For example Figure 6 is an epr spectrum, with no gradient applied, of nylon damaged by X-ray irradiation. The complicated lineshape is due to the hyperfine interaction between the magnetic nuclei of the polymer and the electronic spins. It is obvious that the application of a field gradient to this would simply make a more complicated spectrum without giving significant information as to the distribution of damage in the system.



DPPH

(2,2-Diphenyl-1-picrylhydrazyl)

Fig. 3 Molecular structure of the stable organic free radical used to produce spin phantoms.

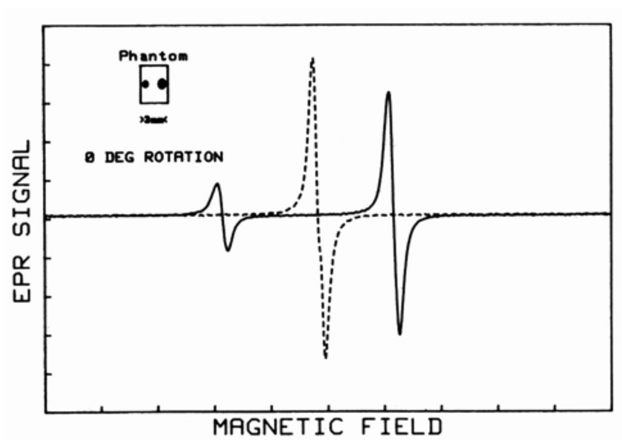


Fig. 4 EPR spectrum of spin phantom with (-----) and without (- - -) an applied field gradient.

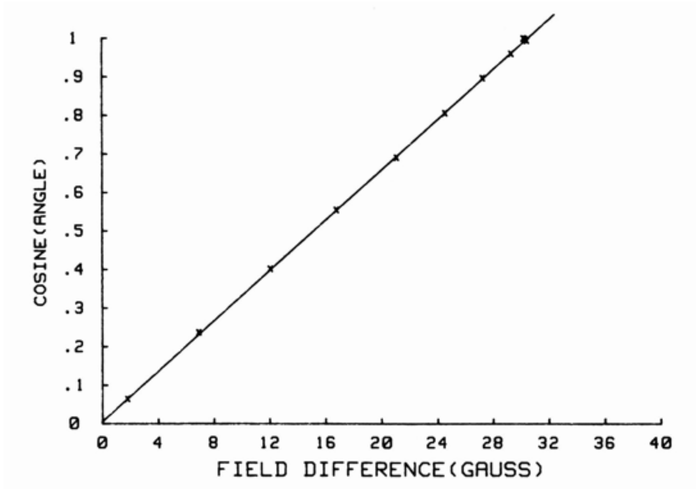


Fig. 5 Angular dependence of peak separation.

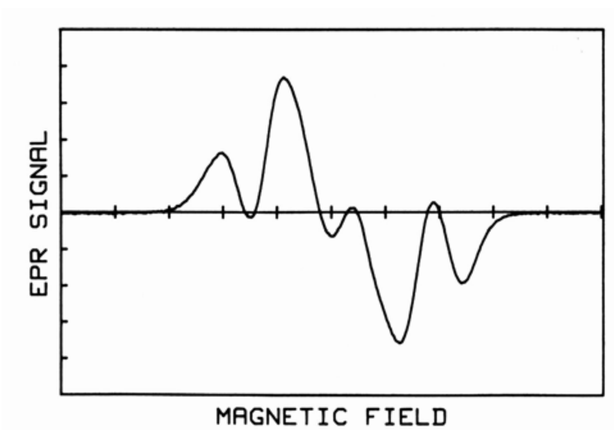


Fig. 6 EPR spectrum of X-ray damaged nylon.

This type of spectral complexity can be handled mathematically by using deconvolution techniques. One technique that is easy and fast to use is based on the convolution theorem of Fourier transforms. Mathematically the spectrum with gradient applied is given by

$$S_g(h) = \int_{-\infty}^{\infty} S_o(h-h')\,\varrho(h')\,dh'$$

where $S_o(h-h')$ is the spectrum obtained in the absence of field gradient and $\rho(h')$ is the spin density in the object. The convolution theorem states that the Fourier transform of the spectrum with applied gradient is equal to the product of the Fourier transforms of the spectrum without the gradient and the spin density i.e.,

$$\mathcal{F}\{S_g(h)\} = \mathcal{F}\{S_o(h)\} * \mathcal{F}\{\varrho(h)\}$$

From this it follows that the spin density can be obtained by taking the inverse Fourier transform of the quotient of the Fourier transforms of $S_G(h)$ and $S_O(h)$ i.e.,

$$\varrho(h) = \mathcal{F}^{-1}\left\{\frac{\mathcal{F}\{S_g(h)\}}{\mathcal{F}\{S_o(h)\}}\right\}$$

This mathematical technique allows one to readily deal with complex lineshapes and to subtract out the intrinsic linewidth of simply-shaped lines.

After the spin density in the sample has been derived as a function of angle in one plane, an orthogonal set of field gradient coils are employed to measure spin density perpendicular to this plane. All of the projections of spin density are subsequently used in an image reconstruction process to generate a three-dimensional image of damage in a material.

The two classes of image reconstruction methods in the greatest use today are the algebraic reconstruction techniques (ART) [5] and Fourier methods [6]. In the algebraic methods the reconstruction space is divided into nonoverlapping elements and iterative techniques are used to match the sums of the reconstruction elements with the projection data. The Fourier methods make use of the projection slice theorem that states that the one-dimensional Fourier transform of a projection at an angle θ is equal to the Fourier transform of the original two-dimensional data evaluated along the angle θ in two-dimensional Fourier space.

The algebraic reconstruction technique has been used with a limited amount of data to generate the two-dimensional plot of spin density of the two spot phantom. This result is displayed in Figure 7. With improved angular resolution and enhanced image processing software the image quality will surely be improved.

In summary, the basis of the epr imaging technique for polymeric and composite materials is the creation of free radicals when a polymer is damaged. These free radicals are trapped by species that are added to the polymer so that a well conditioned signal is obtained. Field gradient coils are employed on an epr spectrometer to map out the spatial extent of damage in the material. Mathematical techniques are employed to lead to a technique that has good sensitivity, high resolution and good contrast.

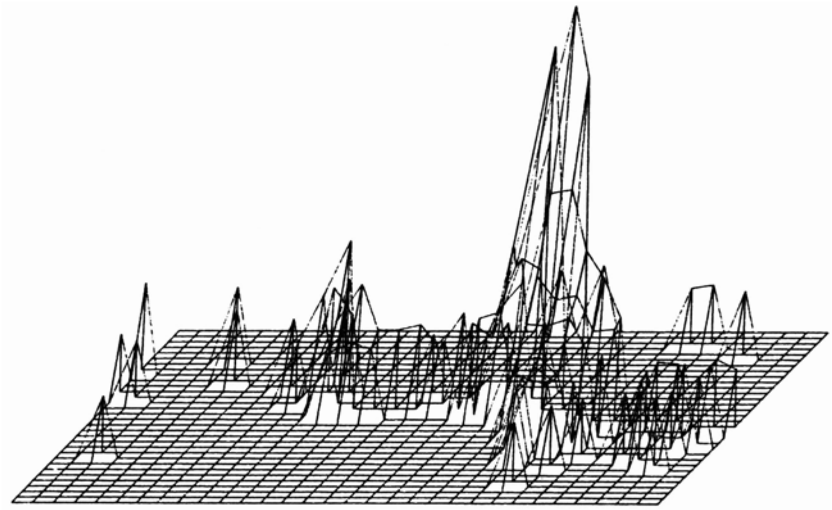


Fig. 7 Image reconstruction using Algebraic Reconstruction Techniques.

ACKNOWLEDGEMENT

This work was supported in part by the Naval Sea Systems Command under Contract No. N00024-85-C-5301.

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